Synthesis, Crystal Chemistry, and Electrochemical Properties of Li$_{7-2x}$La$_3$Zr$_{2-x}$Mo$_x$O$_{12}$ ($x=0.1-0.4$): Stabilization of the Cubic Garnet Polymorph via Substitution of Zr$^{4+}$ by Mo$^{6+}$

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Supporting Information

ABSTRACT: Cubic Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) garnets are exceptionally well suited to be used as solid electrolytes or protecting layers in “Beyond Li-ion Battery” concepts. Unfortunately, cubic LLZO is not stable at room temperature (RT) and has to be stabilized by supervalent dopants. In this study we demonstrate a new possibility to stabilize the cubic phase at RT via substitution of Zr$^{4+}$ by Mo$^{6+}$. A Mo$^{6+}$ content of 0.25 per formula unit (pfu) stabilizes the cubic LLZO phase, and the solubility limit is about 0.3 Mo$^{6+}$ pfu. Based on the results of neutron powder diffraction and Raman spectroscopy, Mo$^{6+}$ is located at the octahedrally coordinated 16$a$ site of the cubic garnet structure (space group Ia-3d). Since Mo$^{6+}$ has a smaller ionic radius compared to Zr$^{4+}$ the lattice parameter $a_0$ decreases almost linearly as a function of the Mo$^{6+}$ content. The highest bulk Li-ion conductivity is found for the 0.25 pfu composition, with a typical RT value of 3.4 × 10$^{-4}$ S cm$^{-1}$. An additional significant resistive contribution originating from the sample interior (most probably from grain boundaries) could be identified in impedance spectra. The latter strongly depends on the prehistory and increases significantly after annealing at 700 °C in ambient air. Cyclic voltammetry experiments on cells containing Mo$^{6+}$ substituted LLZO indicate that the material is stable up to 6 V.

1. INTRODUCTION

Li$_7$La$_3$Zr$_2$O$_{12}$ garnet (LLZO) and its variants are exceptionally well suited for use as electrolytes in “Beyond Li-ion Battery” concepts that employ Li-metal anodes and high voltage cathode materials to enable cells with high energy and power densities. LLZO crystallizes either with tetragonal (I$4$/acd) or cubic (Ia-3d) symmetry (see Figure 1). From the thermodynamic point of view, tetragonal LLZO, which shows a total Li-ion conductivity (reciprocal of the sum of the bulk and grain boundary resistance, for resistive grain boundaries only) that is approximately 2 orders of magnitude lower (<10$^{-6}$ S cm$^{-1}$) than that of the cubic modification (10$^{-9}$ to 10$^{-3}$ S cm$^{-1}$), is the more stable polymorph at room temperature (RT). Fortunately, the cubic phase can be stabilized at RT by supervalent partial substitution of Li$^+$, La$^{3+}$, or Zr$^{4+}$. However, the substituents that induce this phase transition may strongly influence the Li-ion diffusivity and therefore the Li-ion conductivity. Much effort has been undertaken to understand these effects. Allen et al. investigated Li$_{5.75}$La$_3$Zr$_{1.75}$Ta$_{0.25}$O$_{12}$ (LLZTO) garnets substituted with Al or Ga and compared them to the parent compound. LLZTO had Li-ion conductivity that was twice as high (8.7 × 10$^{-4}$ S cm$^{-1}$) as garnets substituted with Al$^{3+}$ (3.7 × 10$^{-4}$ S cm$^{-1}$) or Ga$^{3+}$ (4.1 × 10$^{-4}$ S cm$^{-1}$). They argued that the substituents located at the 24$d$ and/or 96$h$ sites of the Li-ion sublattice possibly had a blocking effect on diffusion in the garnet structure. Recently several of us evaluated this assumption by studying the Li-ion diffusivity of Li$_{7-x}$Ga$_x$La$_7$Zr$_2$O$_{12}$ samples as a function of the site occupancy behavior of Al$^{3+}$ and Ga$^{3+}$.

It was shown that Ga$^{3+}$ as well as Al$^{3+}$ occupies both the 24$d$ and 96$h$ sites, but the blocking effect on Li-ion conductivity seemed to be much weaker than the influence of the unit-cell parameter $a_0$. Nevertheless, there is some interference with Li-ion diffusivity when the Li$^+$ sites are occupied with multivalent ions, as shown recently. Therefore, effort is now being redirected toward finding suitable supervalent ions replacing La$^{3+}$ or Zr$^{4+}$ instead of Li$^+$. Here, we present the possibility of

Received: August 20, 2015
Published: October 9, 2015
stabilizing the cubic LLZO polymorph through the partial substitution of Zr4+ by Mo6+. Li2-xLa1/2Zr2-xMo0.5O3 garnets (abbreviated Zr2−xMo0.5O3) garnets with x = 0.10−0.40 were synthesized by using solid state sintering methods. The samples were carefully characterized in terms of crystal chemistry, morphology, and electrochemical properties (e.g., Li-ion conductivity, interfacial resistivity versus Li-metal electrodes, and the voltage stability window) by means of X-ray powder diffraction (XRPD), neutron powder diffraction (NPD), scanning electron spectroscopy (SEM), Raman spectroscopy, electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV).

2. EXPERIMENTAL SECTION

2.1. Synthesis. The synthesis of Li1−xLa1/2Zr2−xMo0.5O3 garnets with x = 0.10−0.40 was performed by high-temperature sintering. The starting materials were Li2CO3 (99%, Merck), La2O3 (99.99%, Aldrich), ZrO2 (99.9%, Aldrich), and MoO3 (99.98%, Aldrich). Li2CO3 was mixed with the various oxides in the desired proportions and intimately ground together using a hand mortar, a pestle, and isopropanol alcohol. These mixtures were uniaxially pressed into pellets, calcined at 850 °C for 4 h with a heating rate of 5 °C/min, and then cooled in the furnace to approximately 200 °C. Samples mixed with isopropanol alcohol were milled in a Fritsch Pulverisette 7 ball mill for 2 h (12 times 800 rpm for 5 min + 5 min break). Finally, powders were isostatically pressed (24 kbar) to form pellets and sintered at 1230 °C for 4 h, with a heating rate of 20.5 °C/min, and afterward cooled to RT.

2.2. XRPD. XRPD measurements were performed using a Bruker D8 Advance DαVinci Design diffractometer (Xalysse solid state detector) with Cu Kα radiation. This was done in order to characterize the synthetic products and to identify all phases present, including determination of the symmetry and unit-cell dimension of the garnets. Data were collected between 10° and 140° 2θ. The lattice parameter a0 was determined by using an internal standard (Si with a0 = 5.43088 Å) and performing Rietveld refinement with the program Topas V4.2 (Bruker AXS).

2.3. NPD. The neutron diffraction experiment was done at the Institut Laue-Langevin, ILL, in Grenoble (France). Powder diffraction data were acquired in constant wavelength mode (λ = 1.594 Å) using the D2B diffractometer on an 8.5 g batch contained in a 14 mm diameter vanadium sample can at 25 °C. Experiments were performed in the range 5.8° ≤ 2θ ≤ 159.7°, step width 0.04°. Data treatment and refinement were done using the FULLPROF-suite of programs with the pseudo-Voigt peak shape function. Due to the significant absorption of neutron radiation by Li an absorption correction was applied. The atomic displacement parameters were modeled in the isotropic form, except for the oxygen atom; any refinement with anisotropic displacement parameters of the other sites led to non-positive definite atomic displacement parameters and high correlations with the occupation numbers, thus unphysical data.

2.4. SEM. SEM analysis was made using a ZEISS Ultra Plus device. Small polycrystalline chips, taken from the larger pellets, were embedded in an epoxy holder, and the surface was ground and then polished using diamond paste. For the analysis, special attention was paid with regard to extra phases, grain sizes, grain boundaries, and textures using a backscattered electron detector (BSE). Energy dispersive spectroscopy (EDS) measurements were undertaken to measure the atomic ratios of La, Zr, and Mo to determine qualitatively the upper incorporation limit of Mo in LLZO.

2.5. Raman. RAMAN spectra were recorded at RT in the spectral range of 50−800 cm−1 using a Thermo DXR Raman microscope with a 10 mW internal laser light source with excitation wavelength at 780 nm.

2.6. EIS. EIS measurements were carried out to investigate the Li-ion conductivity. Pt thin films were used as electrodes and were sputter deposited with a thickness of 200 nm on top of ca. 10 nm Ti, which improved the adhesion between the sample and the electrode. For the EIS measurements, a Novocontrol Alpha analyzer was used in the frequency range of 3 × 10−5−10 Hz. A Julabo F-25 HE circulator was employed for cooling and heating the samples under investigation. Set temperatures between −12 and 25 °C (with some measurements at 40 °C) were used, leading to true sample temperatures from ca. −8 to 36 °C. In the following, true sample temperatures, measured by a thermocouple, are indicated in all diagrams. An additional impedance spectrum was taken for a Li/garnet/Li sample at RT in an Ar glovebox. For this, metallic lithium was first applied on the surfaces of a pellet and the pellet was sandwiched with two lithium foil disks in a Swagelok type cell (see ref 18).

2.7. CV. CV measurements were performed using a Li/garnet/Au configuration to assess the electrochemical window of garnet pellets. The Au blocking electrode was sputtered on one surface of the garnet pellet, and the reversible Li electrode was applied on the other side of the pellet. Ni foam was used as current collectors. The measurement was carried out inside an Ar glovebox. The cell was scanned at a rate of 2 mV/min in the potential range from −0.5 to 6 V vs Li/Li+.

3. RESULTS AND DISCUSSION

3.1. Phase Composition of the Solid Solutions Studied by XRPD. The dense pellets obtained after the final sintering step were slightly yellowish in color, and after grinding the powder showed a white color. The XRPD patterns of Zr2−xMo0.5O3 garnets with x = 0.10−0.40 are shown in Figure 2 together with reference XRPD patterns for cubic and tetragonal structures.1,2 Sample Zr1.90Mo0.10 exhibits reflections indicating that both cubic (~75%) and tetragonal (~25%) garnets are present. By increasing the amount of Mo6+ to 0.20 pfu the amount of the cubic phase increased (~83%) whereas the tetragonal phase decreased (~17%). With a Mo6+ content of 0.25 pfu no phases other than cubic LLZO were found in the synthetic product. When the Mo6+ content was 0.3 pfu and above, a mixture of extra phases (Zr1.70Mo0.30; La2Zr2O7, La2O3, LiLa(MoO4)2, Li5MoO5Si, Zr1.65Mo0.40; La2Zr2O7, La2O3, LiLa(MoO4)2, Li5MoO5Si) appeared in addition to the cubic LLZO in the product and increased as the Mo6+ content rose.

3.2. Morphology and Phases as Studied by SEM Methods. BSE photos of polycrystalline chips of the samples are shown in Figure 3.

The sample Zr1.90Mo0.10 has large porous and poorly connected grains with diameters of about 100 μm. With a Mo6+ content of 0.2 pfu, the grain size decreased to about 50 μm. Compared to Zr1.90Mo0.10, the sample seemed to be denser, and grains were better connected to each other. Sample
Zr_{1.75}Mo_{0.25} showed a significant increase of the grain sizes (in the range of 200 μm), which may be related to the overall stabilization of the cubic phase. The samples showed less porosity, but there were still large voids between grains. With a Mo^{6+} content of ≥0.3 pfu, smaller grains (50–100 μm) were found and extra phases occurred (see Figures 2 and 3). The density decreased and the porosity within the grains increased with higher Mo^{6+} and impurity content. The qualitative chemical analyses on the polished cross sections of several grains using EDS are consistent with the substitution of Zr^{4+} by Mo^{6+} and an upper incorporation limit close to 0.3 Mo pfu (e.g., Zr_{1.70}Mo_{0.30} ≈ La_{3.00}Zr_{1.70}Mo_{0.28} and Zr_{1.60}Mo_{0.40} ≈ La_{3.04}Zr_{1.76}Mo_{0.30}).

3.3. Unit-Cell Parameter of LLZO as a Function of the Mo^{6+} Content as Studied by Diffraction Methods.

The unit-cell parameters of the cubic LLZO phases, \( a_0 \), as a function of the amount of Mo^{6+} in LLZO are shown in Figure 4. There is a decrease in \( a_0 \) with increasing Mo^{6+} content with an almost linear relationship between \( x = 0.20 \) and 0.30. The decrease of \( a_0 \) can be related to (i) the smaller ionic radius of Mo^{6+} (\( r^{VI} = 0.60 \) Å) compared to Zr^{4+} (\( r^{IV} = 0.72 \) Å) and/or (ii) the reduction of the Li\(^+\) content (Mo^{6+} ↔ Zr^{4+} + 2Li\(^+\)). The unit-cell parameters are on the average around 12.964 Å, which has recently been proposed to be the optimum for high ionic conductivities. Because the unit-cell parameter remained unchanged at a Mo^{6+} content of 0.4 pfu, we assume an upper incorporation limit of about 0.3 Mo^{6+} pfu, which is in agreement with the EDS results (see section 3.2 above).

3.4. Site Occupation Behavior in LLZO: Long-Range Properties as Studied by NPD.

As shown by XRPD and SEM (see section 3.2 and section 3.3 above) the Zr_{1.75}Mo_{0.25} is the only composition that is composed of cubic polymorph only and was therefore used for the NPD study. The Rietveld refinement results of the NPD pattern shown in Figure 5 and given in Table 1 give strong evidence that Mo^{6+} mainly substitutes Zr^{4+} at the octahedral 16\(a\) site, yielding 0.256(2) Mo^{6+} pfu, a value which perfectly matches the nominal stoichiometry; tests with Mo^{6+} on the La^{3+} site gave negative occupation numbers, excluding this site for substitution. In a first model of cationic distribution, the tetrahedral 24\(d\) site is exclusively occupied by Li\(^+\), thereby giving an approximately half filled occupation, the remaining being empty, while the interstitial octahedral coordinated 96\(h\) position hosts about 4.34(2) Li\(^+\) pfu. It might be noted, however, that, with this model, the Rietveld refinements yield a formula that is not balanced in charge but has a deficit of about 0.63 positive charges, probably as Li\(^+\) content. Allowing anisotropic refinement of all atoms, by using non-positive definite displacement parameters, did not significantly change the occupation numbers on 16\(a\) and 24\(d\) sites, but increased that of the 96\(h\) site to 0.42(4), distinctly reducing the deficit in positive charge. It is assumed that the isotropic handling of atoms fails to...
possible to put Mo\(^{6+}\) on the tetrahedral site and obtain a negative scattering length (Mo has a positive one), it is also possible to put Mo\(^{6+}\) on the tetrahedral site, giving a realistic Mo\(^{6+}\) content. The models are diagnostically high Mo\(^{6+}\) of 0.7 pfu and Li contents that are too low, the cubic and tetragonal polymorph. In the range between 600 and 800 cm\(^{-1}\), two \(\text{iso}(\text{Zr})\) bands are observable which correspond most probably to Zr\(^{4+}\) and Mo\(^{6+}\) in LLZO occupying the 6-fold coordinated 16a site in the oxygen garnet framework.

Because of overlapping features in the Raman spectra of probably undetected small amounts of luminescing extra phases, the spectra were baseline corrected and analyzed for qualitative analysis only. A Raman spectroscopy study of LLZO has been reported by Tietz et al.\(^{10}\) The partial substitution of Zr\(^{4+}\) with Ta\(^{5+}\) was investigated later on by Thompson et al.\(^{10}\) They proposed that the band near 650 cm\(^{-1}\) was related to the stretching of the ZrO\(_6\) octahedra. When Ta\(^{5+}\) was added to the system, an additional band near 750 cm\(^{-1}\) appeared and increased in intensity with higher amounts of Ta\(^{5+}\).\(^{10}\) Because bands near 750 cm\(^{-1}\) seem to correspond to stretching of an octahedron other than ZrO\(_6\) the analogous band in our spectra was assigned to a MoO\(_6\) octahedron. This gives additional evidence for the site occupancy of Mo\(^{6+}\) at the octahedral 16a site in the oxygen garnet framework. Because Raman spectroscopy can be used to distinguish cubic and tetragonal LLZO phases, the method can also be used to check phase composition. Tietz et al. showed that the bands near 110 cm\(^{-1}\) are most diagnostic of this.\(^{10}\) The reduction of symmetry from cubic to tetragonal is shown by a splitting of the vibrational modes. In our samples, this feature is not well resolved because of the broad line shape. Nevertheless, it appears that the line shape of those modes at about 110 cm\(^{-1}\) converge with increasing Mo\(^{6+}\) content. This is similar to the observations made by Thompson et al. for Li\(_{0.68}\)La\(_{3}\)Zr\(_{0.75}\)Ta\(_{0.25}\)O\(_{12}\) garnets with increasing amount of Ta\(^{5+}\) up to 0.25 Ta\(^{5+}\) pfu. Above this, they found a superposition of the cubic as well as tetragonal phase in the products. The Raman spectrum of the product with a Mo\(^{6+}\) content of 0.25 in this study looks almost identical to the spectrum reported for single phase cubic Li\(_{0.68}\)La\(_{3}\)Zr\(_{0.75}\)Ta\(_{0.25}\)O\(_{12}\).\(^{11}\) The substitution of Zr\(^{4+}\) by 0.5 Ta\(^{5+}\) or by 0.25 Mo\(^{6+}\) pfu leads to a perfectly tetragonal pattern.

### Table 1. Neutron Powder Diffraction Data of Li\(_{7-x}\)La\(_x\)Zr\(_{0.25}\)Mo\(^{6+}\)O\(_{12}\) Determined through Rietveld Refinement\(^{6}\)

<table>
<thead>
<tr>
<th>site</th>
<th>(x/a, y/b, z/c)</th>
<th>(U_{iso})</th>
<th>occ(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(_1)</td>
<td>24d 0, 3/4, 5/8</td>
<td>3.05(5)</td>
<td>0.50(2)</td>
</tr>
<tr>
<td>Li(_2)</td>
<td>96h 0.0996(1), 0.6829(1), 0.5834(1)</td>
<td>4.2(5)</td>
<td>0.362(1)</td>
</tr>
<tr>
<td>La(_4)</td>
<td>24c 0, 1/4, 1/8</td>
<td>1.54(5)</td>
<td>1.0000</td>
</tr>
<tr>
<td>Zr(_{16})</td>
<td>0, 0, 0</td>
<td>1.71(5)</td>
<td>0.87138</td>
</tr>
<tr>
<td>Mo(_{16})</td>
<td>0, 0, 0</td>
<td>1.71(5)</td>
<td>0.12864</td>
</tr>
<tr>
<td>O(_{96})</td>
<td>-0.03125(1), 0.05544(1), 0.1489(1)</td>
<td>2.18(9)</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

\(^{6}\)Space group: Ia-3d (No. 230) and \(Z = 8\). Lattice parameter: \(a = b = c = 12.9556(2)\). R-factors: \(R = 2.6685, \chi^2 = 1.9451, R_i = 4.1824\). \(^{10}\)Constraint on isotropic atomic displacement: \(U_{iso}(Zr) = U_{iso}(Mo)\). (A trustmark for peak positions of all possible Bragg reflections of cubic LLZO (black) and an unknown Li-containing extra phase, which remain undetected by other analytical methods (red); (inset) crystal structure of cubic LLZO (Ia-3d) based on the results of Rietveld refinement given in Table 1.

Figure 5. Observed (obs), calculated (calc), and difference patterns (obs-calc) for the Rietveld refinement from neutron powder diffraction of nominal Li\(_{6.50}\)La\(_3\)Zr\(_{1.75}\)Mo\(_{0.25}\)O\(_{12}\). The short vertical lines below the profiles mark the peak positions of all possible Bragg reflections of cubic LLZO (black) and an unknown Li-containing extra phase, which remain undetected by other analytical methods (red); (inset) crystal structure of cubic LLZO (black) and an unknown Li-containing extra phase, which remain undetected by other analytical methods (red); (inset) crystal structure of cubic LLZO (Ia-3d) based on the results of Rietveld refinement given in Table 1.
to a decrease in the Li⁺ content to about 6.5 pfu, which also seems to be necessary to stabilize the cubic garnet phase.

3.5.1. Investigating the Li-Ion Conduction in Mo⁶⁺ Doped LLZO by Means of Impedance Spectroscopy. Impedance spectra were measured for as-prepared samples of all compositions at different temperatures. Figure 7 displays the relevant data, measured at RT = 23.5 °C (a) and lowest temperature (ca. −6 °C, a,b). For both temperatures, different magnifications are shown and solid fit lines (equivalent circuit model in Figure 8) are included. Data reflects resistivity, ρ (normalized to the sample area and thickness).

In certain frequency range it can be described by a resistor in parallel to a constant phase element (CPE) with impedance

$$Z_{\text{CPE}} = \frac{1}{(i \omega)^n Q}$$  \hspace{1cm} (1)

where ω is the angular frequency and Q and n are fit parameters. This electrode equivalent circuit helps with analysis of the sample-specific high frequency features but does not imply any mechanistic information. A discussion of the exact electrode reaction mechanisms causing this feature (diffusion or charge transfer processes etc.) is beyond the scope of this paper.

The high frequency arc is attributed to the bulk Li-ion conduction (σ bulk) of the LLZO samples; see also the discussion of capacitances below. For a proper fit analysis of the σ bulk and permittivity (ε) another resistor (R₁) in parallel to a constant phase element (CPE) was used.

Capacitances were then calculated from fit parameters Q₁ and n₁ according to ref12:

$$C_1 = (R_1^{1-n_1} Q_1)^{1/n_1}$$  \hspace{1cm} (2)

Particularly for samples with low bulk resistances (R₁), the unavoidable inductance (L) due to wiring significantly affects the data and has to be added to the equivalent circuit. Finally, a proper description of the partial intermediate frequency feature is necessary to obtain a reliable fit of the spectra and thus of the σ bulk. As required, e.g., for Zr₁.75Mo⁰.25, Zr₁.70Mo⁰.30 and Zr₁.60Mo⁰.40, this feature was again approximated by a resistor in parallel to a constant phase element. A mechanistic discussion of this second (i.e., intermediate frequency) arc is given below. The resulting equivalent circuit is shown in Figure 8 and fits all measurement data acceptably well; fit examples are shown in Figures 7, 8, and 9.

3.5.2. Objections to the Impedance Data Analysis. Two possible objections to such a data analysis are considered: First, one may question the appropriateness of a R-CPE element for describing partly almost horizontal line in the intermediate frequency range. Here, an additional phenomenon comes into play. After annealing the samples at 700 °C for a few minutes
applying this model to spectra obtained on as-prepared Zr1.75Mo0.25 describes the data very well, supporting the approach of consistent capacitance and resistance data can be obtained. However, when starting the fitting procedure at low temperatures and always using the fit results as starting values of the next fit procedure at the next higher temperature, very consistent capacitance and resistance data can be obtained (see below). Capacitances from CPE1 did not vary too much, and conductivities close to RT are in line with those extrapolated from the very reliable low temperature conductivity data. Additional evidence for the meaningfulness of this analysis comes from a measurement performed on Zr1.75Mo0.25 of a different batch series with reversible Li electrodes, see below. Hence, we consider this analysis as meaningful and able to deduce the proper bulk materials parameters.

3.5.3. The Bulk Transport of Li-Ions in Mo-Doped LLZO. A strong argument in favor of Rb representing a bulk transport process is the existence of a meaningful geometrical bulk capacitance in parallel. C1 values are in the 10 pF range, and calculating a relative permittivity \( \varepsilon_{r,1} \) from sample area A and sample thickness \( d \) (\( \varepsilon_0 \) = vacuum permittivity) according to

\[
\varepsilon_{r,1} = \frac{C_1 d}{A \varepsilon_0}
\]

leads to values of the order of 40–60. The relative permittivities for all temperatures and samples before and after annealing are summarized in Figure S2. The increase close to RT, found for some samples, reflects the uncertainty due to absence of large parts of the high frequency arcs. The \( \varepsilon_{r,1} \) values of ca. 40–60 are very realistic bulk values for oxides with significant ionic polarization (and similar to \( \varepsilon_{r1} \) of ZrO2) and thus support the interpretation of \( R_b \) as a bulk property. We cannot exclude the existence of highly conducting grain boundaries, since those would only add an additional resistor in parallel to \( R_b \) and thus do not change the shape of the spectrum and the capacitance. However, to date conclusive experimental evidence supporting the assumption of fast grain boundary conduction in LLZO is not available in the literature. Accordingly, the bulk conductivity, \( \sigma_{bulk} \) of Li-ions in our LLZO samples was determined from \( R_b \) by

\[
\sigma_{bulk} = \frac{d}{R_b A}
\]

Arrhenius plots of the Li-ion conductivities are shown in Figure 11 for all samples before (a) and after annealing (b). Data scattering can be largely attributed to fitting inaccuracies caused by the intermediate frequency arc (see above). Before annealing (as-prepared), Li-ion conductivities of most compositions (except Zr1.90Mo0.10) coincide at RT. All Arrhenius fits lead to ca. 3.4 × 10^{-4} S cm^{-1}; exact values are given in Table 2.
Slight differences in activation energies $E_a$ (see Table 2) cause some discrimination at low temperatures with $\text{Zr}_{1.75}\text{Mo}_{0.25}$ exhibiting the highest low temperature Li-ion conductivity. Annealing at 700 °C leaves the $\sigma_{\text{bulk}}$ of $\text{Zr}_{1.80}\text{Mo}_{0.20}$ and $\text{Zr}_{1.75}\text{Mo}_{0.25}$ virtually identical ($\sim 3.4 \times 10^{-4}$ S cm$^{-1}$) at RT, with the best low temperature $\sigma_{\text{bulk}}$ found for $\text{Zr}_{1.75}\text{Mo}_{0.25}$.

The samples $\text{Zr}_{1.70}\text{Mo}_{0.30}$ and $\text{Zr}_{1.60}\text{Mo}_{0.40}$ exhibit a drop in conductivity by ca. a factor of 2. This decrease of Li-ion conductivity may be related to phase changes since those samples are not phase-pure. The $E_a$ values of $\sigma_{\text{bulk}} \cdot T$ are in the range of 0.36–0.49 eV (see Table 2), and the best Li-ion conducting composition ($\text{Zr}_{1.75}\text{Mo}_{0.25}$) exhibits the lowest value (0.39 eV as-prepared and 0.36 eV after annealing, respectively). All other samples have very similar activation energies with an average of ca. 0.45 eV. Activation energies are thus compatible with other Li-oxide garnets. See also Figures S3 and S4 for further discussion, particularly of $\sigma_{\text{bulk}}$ variations of nominally identical samples from different batches.

### 3.5.4. The Intermediate Frequency Arc: Grain Boundary or Not?

Intermediate frequency impedance features are often found in the literature and are sometimes interpreted in terms of resistive grain boundaries. In other cases, an additional arc in the spectrum is attributed to the electrode/LLZO interface. For a more detailed analysis of the intermediate frequency arcs observed in the Nyquist plots of the samples in this study, analysis of the corresponding capacitance is helpful. This may give information on the location of the resistor $R_2$.

Here, eq 3 cannot simply be applied to $C_2$ since the relevant thickness is unknown; in case of one-dimensional current flow we should use the thickness of the region(s) causing the resistance.

In a first approach, we may assume bulk permittivity also for $C_2$, and then an effective thickness $d_2$ of the corresponding resistive regions can be determined. This type of analysis is very common for grain boundaries (brick layer model) and leads to the thickness values shown in Figure 12. The nominal thickness $d_2$ strongly varies between samples, and a systematic

![Figure 11. Temperature dependent bulk conductivities for as-prepared (a) and annealed (b) samples of different Mo doping content.](image)

### Table 2. Activation Energies, $E_{a1}$ (Bulk) and $E_{a2}$ (Intermediate Arc), of $\sigma_{\text{bulk}} \cdot T$ and Bulk Conductivities, $\sigma_{\text{bulk}}$, of $\text{Zr}_{2-x}\text{Mo}_x$ with $x = 0.0–0.4$ at RT According to the Arrhenius Fit

<table>
<thead>
<tr>
<th>x</th>
<th>$E_{a1}^m$ [eV]</th>
<th>$E_{a2}^m$ [eV]</th>
<th>$E_{a1}^m$ [eV]</th>
<th>$E_{a2}^m$ [eV]</th>
<th>$\sigma_{\text{bulk}}^m$ [S cm$^{-1}$]</th>
<th>$\sigma_{\text{bulk}}^m$ [S cm$^{-1}$]</th>
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<tbody>
<tr>
<td>0.10</td>
<td>0.46</td>
<td>0.48</td>
<td>0.44</td>
<td>0.44</td>
<td>8.00 × 10$^{-5}$</td>
<td>6.82 × 10$^{-5}$</td>
</tr>
<tr>
<td>0.20</td>
<td>0.48</td>
<td>0.44</td>
<td>0.44</td>
<td>0.44</td>
<td>3.11 × 10$^{-4}$</td>
<td>3.38 × 10$^{-4}$</td>
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<tr>
<td>0.25</td>
<td>0.39</td>
<td>0.36</td>
<td>0.44</td>
<td>0.43</td>
<td>3.33 × 10$^{-4}$</td>
<td>3.40 × 10$^{-4}$</td>
</tr>
<tr>
<td>0.30</td>
<td>0.49</td>
<td>0.44</td>
<td>0.40</td>
<td>0.56</td>
<td>3.69 × 10$^{-4}$</td>
<td>4.00 × 10$^{-4}$</td>
</tr>
<tr>
<td>0.40</td>
<td>0.43</td>
<td>0.65</td>
<td>0.65</td>
<td>0.66</td>
<td>3.40 × 10$^{-4}$</td>
<td>1.58 × 10$^{-4}$</td>
</tr>
</tbody>
</table>

*Activation energies of the intermediate arc, see in the text. *Samples as-prepared are abbreviated ap and samples after annealing an.

Figure 12. Thickness of the region causing the intermediate frequency arc, calculated from $C_2$ by assuming bulk permittivity. (a) Values of as-prepared samples for different temperatures. (b) Values of annealed samples for different temperatures. All open symbols refer to samples for which the exponent $n$ of the CPE element is on average below 0.6. Since bulk capacitances and thus bulk permittivities become less accurate for increasing temperature (see Figure S2), we used the very reliable permittivity determined from the lowest temperature to calculate all $d_2$ values.
trend with annealing is not obvious. However, the constant phase elements $CPE_2$ of several samples exhibit very low exponents (average of $n < 0.6$); those samples are indicated in Figure 12. The most reliable $C_2$ values consistently lead to a thickness $d_2$ of ca. 10–20 μm, independent of annealing.

The corresponding resistive region might be serially distributed within the entire sample (e.g., several serial grain boundaries) or could be located at the two electrode/electrolyte interfaces. In order to further analyze the position, we removed ca. 1/5 of a sample by grinding both sample sides and measured the impedance again (resulting spectrum is shown in Figure S4). Obviously, some changes compared to the originally annealed sample exist, but the intermediate frequency arc is still present and of similar size as before. This suggests that the resistive region is not restricted to a zone near the electrodes, but rather is an effect that includes regions within the entire sample, most probably, the grain boundaries.

The measurement of a Zr$_{1.75}$Mo$_{0.25}$ sample with Li electrodes strongly supports this interpretation. Figure 13 displays the corresponding impedance spectrum. While the high and intermediate frequency arcs are again clearly visible, the low frequency electrode response shrank to a tiny feature at very low frequencies.

The latter is typical for Li electrodes but not further considered here. Two serial R-CPE elements fit the data well (solid line), and interpretation of $R_2$ in terms of the bulk conductivity leads to $\sigma_{bulk} = 2.4 \times 10^{-4}$ S cm$^{-1}$. This is in good agreement with measurements using Pt/Ti electrodes, particularly in consideration of the fact that a sample of a different batch was analyzed and a variation of the conductivity between different batches was also found for Pt/Ti electrodes, see Figure S3.

The capacitance of the intermediate frequency arc can be determined from eq 2, and the resulting value corresponds to a thickness of ca. 7 μm (assuming $\varepsilon_2 \approx \varepsilon_1$ and homogeneous current flow, a Li-ion conductivity of the resistive region (presumably at grain boundaries) can finally be calculated, irrespective of the transport mechanism and location. Arrhenius diagrams of these conductivities are shown for all samples in Figure 14. Activation energies are similar to those of the bulk conductivity, typically in the 0.4–0.5 eV range, partly up to 0.66 eV (see Table 1). Li-ion conductivities at RT are of the order of $10^{-5}$ to $10^{-7}$ S cm$^{-1}$, depending on composition and annealing, and thus many orders of magnitude lower than the Li-ion bulk conductivity. A similar value is found for the Li/garnet/Li sample (ca. $5 \times 10^{-7}$ S cm$^{-1}$). (Note that this is the true conductivity of the resistive zone. When considering effective sample conductivities, the resistance $R_2$ has to be normalized to the entire sample thickness.) The very low conductivity of the resistive zone indicates that it is highly important for any application to understand and ultimately reduce or eliminate this effect.

3.5.5. The Li-Ion Conductivity of Resistive Zones in Mo-Doped LLZO. Assuming the appropriateness of the assumptions $\varepsilon_2 \approx \varepsilon_1$ and homogeneous current flow, a Li-ion conductivity of the resistive region (presumably at grain boundaries) can finally be calculated, irrespective of the transport mechanism and location. Arrhenius diagrams of these conductivities are shown for all samples in Figure 14. Activation energies are similar to those of the bulk conductivity, typically in the 0.4–0.5 eV range, partly up to 0.66 eV (see Table 1). Li-ion conductivities at RT are of the order of $10^{-5}$ to $10^{-7}$ S cm$^{-1}$, depending on composition and annealing, and thus many orders of magnitude lower than the Li-ion bulk conductivity. A similar value is found for the Li/garnet/Li sample (ca. $5 \times 10^{-7}$ S cm$^{-1}$). (Note that this is the true conductivity of the resistive zone. When considering effective sample conductivities, the resistance $R_2$ has to be normalized to the entire sample thickness.) The very low conductivity of the resistive zone indicates that it is highly important for any application to understand and ultimately reduce or eliminate this effect.

3.6. Electrochemical Stability Measured by CV. Finally we checked the electrochemical stability of Mo-doped LLZO. Therefore, a cyclic voltammetry experiment on a Li/ Zr$_{1.75}$Mo$_{0.25}$/Au cell was measured to investigate the electrochemical window of the garnet pellet.

As shown in Figure 15, peaks due to an alloying reaction between Au and Li and extraction of Li from the alloy were clearly observed without obvious peaks at higher voltages, indicating that Li$^+$ could pass through the garnet pellet without possible degradation reactions. During the anodic sweep of the CV experiment, the garnet was found to be stable up to 6 V.

4. CONCLUSION

Cubic Li$_{0.5}$La$_{0.5}$Zr$_{2-x}$Mo$_{x}$O$_{12}$ garnets were synthesized using ceramic sintering methods. Since Mo$^{VI}$ substitutes for twice as
much Li⁺ as Ta⁵⁺ does, about 0.25 Mo⁶⁺ is enough to decrease the Li⁺ content to the critical amount of ≤ 6.5 Li⁺ pfu, which stabilizes the cubic LLZO garnet phase. The solubility limit of Mo⁶⁺ in LLZO is about 0.3 pfu, lower than that of other supervalent ions that substitute for Zr⁴⁺. Mo⁶⁺ has a smaller ionic radius than Zr⁴⁺ and is located at the 16a site of the cubic oxygen garnet framework causing the unit-cell parameter, a₀, to decrease as a function of the Mo⁶⁺ content. The highest σbulk is found for 0.25 Mo⁶⁺ pfu LLZO (ca. 3 × 10⁻⁴ S cm⁻¹ at RT with significant variation for nominally identical samples). An intermediate frequency arc was found in the impedance spectra, and its detailed analysis indicates that it differs from the interface-related additional arc found in some studies on LLZO. Rather, the additional resistance can be associated with resistive zones in the sample, most probably grain boundaries, and lowers the effective Li-ion conductivities. It is thus highly important for any application not only to control the interfacial resistance at the electrodes but also to understand and ultimately reduce or eliminate any additional resistance within the sample. Finally the voltage stability window of Mo⁶⁺ doped LLZO was checked and found to be about 6 V, which enables the use of high voltage cathode materials.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01895.

Results from impedance spectroscopy and bulk permitivities (PDF)

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Funding
The research was supported by Austrian Science Fund (FWF): Project No. P25702.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful to ILL for making all facilities available. The portion of the work performed at LBNL was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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